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The Structure of the Mercury/Dimethylsulfoxide Interface in the Presence of Tetraalkylammonium Perchlorates

by

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The Structure of the Mercury/Dimethylsulfoxide Interface in the Presence of Tetraalkylammonium Perchlorate.

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The structure of the mercury/non-aqueous solution interface has been studied in the presence of a number of aprotic solvents [1, 2]. In the case of dimethylsulfoxide (DMSO), Payne [3] studied the behavior of alkali metal salts with a variety of anions and observed a strong resemblance to the corresponding aqueous systems. On the other hand, the properties of the mercury/DMSO solution interface have not been investigated in the presence of tetraalkylammonium salts in spite of the popularity of these electrolytes in non-aqueous electrochemistry. In this paper, we report a study of double layer structure in the presence of tetraethylammonium perchlorate (TEAP), and the corresponding tetrapropylammonium (TPAP) and tetrabutylammonium salts (TBAP, assess the role of perchlorate anion adsorption, and compare the inner layer capacity curves with those found in other aprotic solvents such as acetonitrile [4] and dimethylformamide [5].

Differential capacity against potential data were obtained using an a.c. impedance bridge with potentiostatic control of the mercury electrode. The potential of zero charge was determined using a streaming mercury electrode. In the case of TBAP, capacity data were collected at ten concentrations in the range 0.013 to 0.10 M. The potential of the Hg electrode was measured with respect to a Ag/Ag^+ reference electrode. The tetraalkylammonium salts and the DMSO were purified using well established procedures.

Differential capacity against potential data for the Hg/TBAP system in DMSO are shown in Fig. 1, the potential scale being referenced to the potential of zero charge (p.z.c.) Diffuse layer minima coincident with the p.z.c. are clearly defined at lower salt concentrations. According to the Gouy-Chapman-Stern model of the double layer, the reciprocal of the double layer capacity at the p.z.c. $1/C_o$ should be linear in the reciprocal of the square root of the electrolyte concentration $1/c_s^{1/2}$ if specific adsorption is absent, the relationship being [4]

$$1/C_o = 1/C_{io} + 1/f\,\Theta\,c_s^{1/2} \qquad (1)$$

C_{io} is the inner layer capacity at the p.z.c., $\Theta^2 = 2RT\varepsilon\varepsilon_o$ where ε is the dielectric constant of DMSO, and $f = F/RT$. Although the relationship is linear (Fig. 2), the slope is not equal to $1/f\,\Theta$ suggesting that weak specific adsorption is present. The presence of specific adsorption can also be tested on the basis of plots of $1/C$ against $1/C_d$ at constant electrode charge density where C_d is the diffuse layer capacity estimated on the basis of Gouy-Chapman theory (see Fig. 3). According to these plots specific adsorption disappears at negative charge densities indicating that the weakly adsorbing species is the perchlorate ion.

As expected, the shape of the capacity-potential curves depends on the nature of the tetraalkylammonium cation at negative charge densities. This dependence is discussed in terms of the relative influence of the cation on the dielectric constant of the inner layer and on its thickness. Finally, the data in DMSO are compared with those obtained earlier in acetonitrile [4] and dimethylformamide [5].

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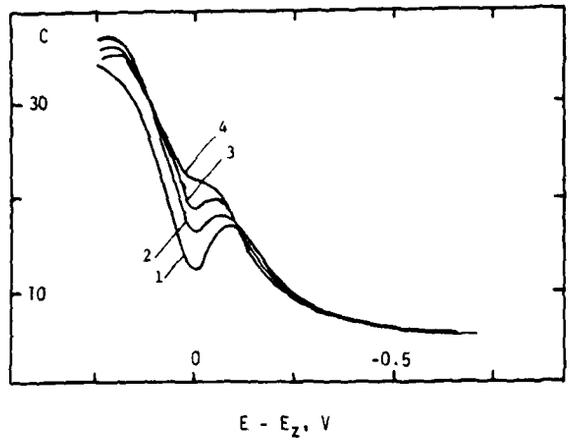

Fig. 1 Differential capacity against potential for the Hg/DMSO interface with varying concentrations of TBAP: 0.013(1), 0.032(2), 0.056(3) and 0.10 M(4).

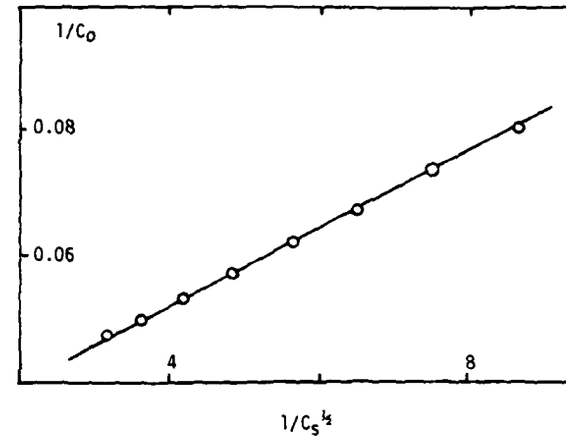

Fig. 2 Reciprocal capacity at the p.z.c. $1/C_o$ plotted against the reciprocal of the square root of salt concentration for the Hg/DMSO interface with TBAP as electrolyte.

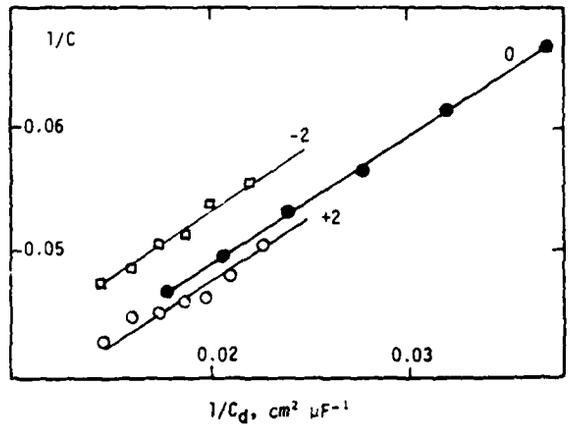

Fig. 3 Reciprocal capacity 1/C against the reciprocal of the diffuse layer capacity $1/C_d$ for constant electrode charge density as indicated. The lines are drawn with unit slope.